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JC20 REC'D-G/PL 11 SEP 2003

DESCRIPTION

COPPER-BASED ALLOY

5 Technical Field:

This invention relates to a copper-based alloy which is suitable for plumbing hardware, such as valves, cocks and joints, and which has been improved in mechanical properties, particularly tensile force, so as to reject otherwise possible deterioration at elevated temperatures.

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Background Art:

Generally, the bronze cast (CAC406) is suitable for casting a product in a fairly complicated shape because it excels in castability, corrosion resistance, machinability and pressure resistance and moreover enjoys ideal flowability in a fused state. It has been being copiously used generally for plumbing hardware, such as valves, cocks and joints.

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Recently, since the Pb (lead) contained in the bronze has been posing a serious social problem of exerting an adverse effect on the human body, an exacting restriction has come to be imposed on the amount of Pb suffered to diffuse into the running tap water even on the global scale.

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On account of this situation, therefore, the development of a new useful leadless copper alloy has become urgently necessary. In the circumstance, various materials of the Bi-, Bi-Sb- and Bi-Se-base are being developed now.

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JP-B HEI 5-63536, for example, proposes a leadless copper alloy which is enabled by having Bi substitute for the lead in the copper alloy to enhance the machinability and preclude the phenomenon of dezincification.

Then, Japanese Patent No. 2889829 proposes a leadless bronze which, by the addition of Sb, is enabled to suppress the occurrence of porosity during the course of casting owing to the addition of Bi aimed at enhancing machinability and acquire enhanced mechanical strength.

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Further, U.S. Patent No. 5614038 proposes a bronze alloy that derives precipitation particularly of a Zn-Se compound from addition of Se and Bi and consequently acquires substantially equal mechanical properties, machinability and castability to the CAC406.

These leadless copper alloys more often than not appropriate for mass production thereof the existing casting facilities used for the production of the conventional CAC406. In this case, the possibility of the products being adulterated with the Pb from the furnace and the ladle is conceivable.

5 Further, the leadless copper alloys are produced by using recycled materials, such as scraps, in due respect of the commercial availability of ingots, the cost and the environment. These materials are inevitably adulterated with Pb as an unavoidable impurity.

10 The leadless copper alloys, therefore, allow a Pb content of not more than 0.4 weight% on the unavoidable impurity level even when the casting facilities are used exclusively for the leadless copper alloys. Such is the true state of affairs.

The leadless bronze cast alloys which add Bi as an alternative element for Pb as disclosed in JP-B HEI 5-63536, Japanese Patent No. 2889829 and U.S. Patent No. 5614038, when containing Pb in such a very small amount as mentioned above, possibly  
15 suffer their mechanical properties, particularly tensile strength, to be deteriorated on exposure to such elevated temperatures as exceeding 100°C.

This possibility is ascribed to the fact that when the leadless bronze cast alloys adding Bi as an alternative component for Pb happen to contain Pb even in a very small amount, the Bi and Pb which avoid forming a solid solution with Cu persist as low-  
20 melting Bi-Pb binary eutectic crystals in the crystal grain boundaries and in the crystal grains and they form locally weak portions and lower the tensile strength at elevated temperatures.

The term "eutectic crystal" as used herein refers to a crystal having a texture formed by the simultaneous precipitation of the crystals of  $\alpha$  and  $\beta$  from the melt. The  
25 crystal grains of this texture are extremely small and form a texture having  $\alpha$  and  $\beta$  in a mixed state.

The decrease of the tensile strength mentioned above does not affect the actual use of the plumbing hardware made of the cast alloys under discussion. The market nevertheless seeks supply of a leadless bronze cast which is capable of acquiring  
30 mechanical properties approximating as much to those of CAC406 as possible.

This invention has been developed in view of the true state of affairs mentioned above and has for an object thereof the provision of a leadless copper-based alloy having the mechanical properties thereof further approximated to the CAC406 by forming in the

alloy texture an alloy or an intermetallic compound with Bi and Pb existing either in independent states or in a mutually joined state, thereby mending the deterioration of the tensile strength at elevated temperatures.

5 Disclosure of the Invention:

A copper-based alloy has incorporated therein an additive element capable of forming an alloy or an intermetallic compound with Bi and Pb existing independently or in a mutually joined state to improve mechanical properties, particularly tensile strength, thereof at elevated temperatures.

10 In the copper-based alloy, the additive element is one or more members selected from the group consisting of Te, P, Zr, Ti, Co, In, Ca, B and misch metal.

In the copper-based alloy, the additive element is contained in a ratio in a range of 0.01 to 2.0 weight%.

15 In the copper-based alloy, it suppresses occurrence of a Bi-Pb binary eutectic crystal in a texture thereof.

In the copper-based alloy, it contains at least Sn in a ratio of 2.8 to 6.0 weight%, Zn in a ratio of 1.0 to 12.0 weight% and Bi in a ratio of 0.1 to 3.0 weight%.

20 In the copper-based alloy, wherein it contains at least Sn in a ratio of 2.8 to 6.0 weight%, Zn in a ratio of 1.0 to 12.0 weight%, Bi in a ratio of 0.1 to 2.4 weight% and Se in a ratio of 0.05 to 1.2 weight%.

In the copper-based alloy, it has a Pb content of not more than 0.25 weight%.

Brief Description of the Drawing

Fig. 1 is a graph showing the results of tensile test 1.

25 Fig. 2 is a graph showing the results of tensile test 2.

Fig. 3 is a graph showing the results of tensile test 3.

Fig. 4 is a graph showing the results of tensile test 3.

Fig. 5 is a graph showing the results of tensile test 3.

Fig. 6 is a graph showing the results of tensile test 4.

30 Fig. 7 is a graph showing the results of a machinability test.

Fig. 8 is a graph showing the results of the Charpy impact test of samples, No.62 to No. 64, and the surface area ratio of Bi-Pb.

Fig. 9 is a graph showing the results of the Charpy impact test of samples, No. 65

to No. 67, and the surface area ratio of Bi-Pb.

Fig. 10 is a metallographic photograph (400 magnifications) of a standard sample (comparative example).

Fig. 11 is a mapping of the component elements appearing in the metallographic photograph of Fig. 10.

Fig. 12 is a metallographic photograph (400 magnifications) of sample No. 63 containing P in a ratio of 0.09 weight%.

Fig. 13 is a mapping of the component elements appearing in the metallographic photograph of Fig. 12.

Fig. 14 is a metallographic photograph (400 magnifications) of sample No. 66 containing Te in a ratio of 0.21 weight%.

Fig. 15 is a mapping of the component elements appearing in the metallographic photograph of Fig. 14.

Fig. 16 is a histolytic photograph (before and after image processing) determining the surface area ratios of samples No. 62 to No. 64.

Fig. 17 is a histolytic photograph (before and after image processing) determining the surface area ratios of samples No. 65 to No. 67.

Best Mode for carrying out the Invention:

The significance of using an additive element forming an alloy or an intermetallic compound with Bi and Pb existing either in independent states or in a mutually joined state in the copper-based alloy of this invention will be described below.

When the alloy incorporates the additive element therein, a Bi-M intermetallic compound (or alloy), a Pb-M intermetallic compound (or alloy), or a Bi-Pb-M intermetallic compound (or alloy) is formed in the alloy texture and enabled to suppress the occurrence of a Bi-Pb binary eutectic crystal in the alloy texture. The symbol M refers to an additive element, which is one or more members selected from the group consisting of Te, P, Zr, Ti, Co, In, Ca, B and a misch metal.

The cast alloy, by containing therein the additive elements, i.e. one or more members selected from the group consisting of Te, P, Zr, Ti, Co, In, Ca, B and misch metal, is enabled during the course of solidification thereof to form the Bi-M intermetallic compound (or alloy), Pb-M intermetallic compound (or alloy) or Bi-Pb-M intermetallic compound (or alloy) having a higher melting point than the Bi-Pb binary eutectic crystal

earlier than the precipitation of the Bi-Pb binary crystal in the alloy texture and consequently decrease the Bi and Pb forming the Bi-Pb binary eutectic crystal in the alloy texture and suppress the occurrence of the Bi-Pb binary eutectic crystal.

By causing the occurrence of the Bi-Pb binary eutectic crystal to be suppressed as  
5 described above, it is made possible to enhance the mechanical properties at elevated temperatures.

The particularly preferred copper-based alloys are Cu-Sn-Zn-Bi- and Cu-Sn-Zn-Bi-Se-based alloys. These copper-based alloys adopt the form of containing the component elements shown below. The individual ranges of these components and the  
10 reasons therefor will be specifically described in detail below.

Sn: 2.8 to 6.0 weight%

This element is contained for the purpose of permitting solid solution in the  $\alpha$  phase, enhancing strength and hardness and enhancing wear resistance and corrosion resistance owing to the formation of a protective film of  $\text{SnO}_2$ . The Sn is an element that  
15 in the range of actual ratio in a composition degrades machinability in accordance as the content thereof is increased. It is, therefore, required to secure mechanical properties in the range in which the content is suppressed and further the corrosion resistance is kept from decreasing. As the more preferred range particularly in terms of the characteristic quality of the elongation which is susceptible of the influence of the Sn content, the range  
20 of 3.5 to 4.5 weight% in which the elongation in the neighborhood of 4.0 weight% promising the best characteristic properties is infallibly attained has been discovered.

Zn: 1.0 to 12.0 weight%

This element is effective in enhancing hardness and mechanical properties, particularly elongation, without affecting machinability. The content effective in  
25 improving characteristic properties at elevated temperatures is found to be not less than 1.0 weight% in consideration of the additive elements, such as Te that forms an alloy or an intermetallic compound with Bi and Pb, and the Sn content. Since the Zn is further effective in suppressing the occurrence of Sn oxide due to the absorption of gas by the melt and ensuring the wholesomeness of the melt, the content of not less than 4.0  
30 weight% is found to be effective in enabling this action to be taken. More practically, the content of not less than 5.0 weight% proves advantageous from the viewpoint of compensating for the proportions of Bi and Se to be suppressed. Since the Zn has a high vapor pressure, the content of not more than 12.0 weight% proves favorable in

consideration of the working atmosphere and the castability. Particularly, the content of about 8.0 weight% proves optimum in consideration of the economy.

Bi: 0.1 to 3.0 weight%

5 The content of not less than 0.1 weight% is found to be effective for the purpose of enhancing the machinability. For the purpose of entering into the porosity formed in the cast product during the course of solidification of the cast alloy, suppressing the occurrence of casting defects, such as shrinkage cavity, and securing the wholesomeness of the cast alloy, the content of not less than 0.6 weight% proves effective. For the purpose of securing necessary mechanical properties, the content of not more than 3.0 weight% proves effective. Particularly, the content of not more than 1.7 weight% proves favorable for the purpose of securing the mechanical properties fully satisfactorily while keeping the content down. It is practically preferable to contain Bi in a ratio in the range of 0.1 to 2.4 weight% in conjunction with Se. The optimum Bi content is about 1.3 weight% in consideration of the optimum content of Se.

15 Se: 0.05 to 1.2 weight%

This element is present in the form of an intermetallic compound of Bi-Se, Zn-Se, or Cu-Se in the copper alloy and constitutes a component for contributing to the securement of machinability and wholesomeness of cast alloy. The containment of Se, therefore, is effective in securing mechanical properties and wholesomeness of cast alloy while suppressing the content of Bi. The upper limit of this content has been fixed at 1.2 weight% from the viewpoint of the economy. Though the Se contributes to the securement of the wholesomeness of cast alloy even when it is contained in a very small amount, the content of not less than 0.05 weight% is effective for the purpose of securing this action infallibly. Thus, this magnitude has been adopted as the lower limit of the content. Particularly, the optimum content is about 0.2 weight%.

25 Te: 0.01 to 1.0 weight%

This element constitutes a component for enhancing machinability by avoiding formation of a solid solution and undergoing dispersion in the matrix. The Te, however, does not manifest the effect of enhancing machinability when the content thereof falls short of 0.01 weight%. The content of not less than 0.05 weight% is favorable for the purpose of inducing crystallization of an intermetallic compound TePb (melting point of about 917°C) and suppressing the occurrence of a Bi-Pb binary eutectic crystal. When the content exceeds 1.0 weight%, the excess results in contradicting economy and failing

to mend the deterioration of tensile strength proportionately to the increase of the content. All these points taken into consideration, the Te content has been specified in the range of 0.01 to 1.0 weight% and preferably in the range of 0.05 to 0.5 weight%.

P: 0.01 to 0.5 weight%

5 This element is contained in a ratio in the range of 0.01 to 0.5 weight% for the purpose of promoting the deacidification of the melt and successfully manufacturing a wholesome cast alloy. When the content exceeds the upper limit of this range, the excess tends to lower the solidus line and induce segregation. The P has the function of refining the crystal grains and enhancing the mechanical properties. When the P is added as a  
10 deacidifying agent, the P content in the alloy generally is in the range of 0.015 to 0.03 weight%. For the purpose of inducing crystallization of an intermetallic compound  $Pb_3P_2$  which has a higher melting point than the Bi-Pb binary eutectic crystal (melting point of about 125°C), suppressing the formation of the Bi-Pb binary eutectic crystal and mending the deterioration of the tensile strength at elevated temperatures, the content is preferred  
15 to be in the range of 0.05 to 0.1 weight%.

Pb: not more than 0.25 weight%

In view of the possibility that the Pb is contained in a ratio in the range of 0.3 to 0.4 weight% even on the impurity level, the content of the Pb as not a positively admissible unavoidable impurity is specified to be not more than 0.25 weight%.

20 Besides the Te and Zr mentioned above, the additive element that the copper-based alloy of this invention is allowed to use for the purpose of suppressing the occurrence of the Bi-Pb binary eutectic crystal is one or more members selected from the group consisting of Te, P, Zr, Ti, Co, In, Ca, B and misch metal. The content of the additive element is preferred to be in the range of 0.01 to 1.0 weight%. As regards the  
25 copper-based alloy containing Sb at a ratio in the range of 0.05 to 0.5 weight%, the use of the aforementioned additive elements is effective in suppressing the occurrence of the Bi-Pb binary eutectic crystal and enhancing the characteristic properties at elevated temperatures. As concrete examples of the unavoidable impurities in the copper-based alloy of this invention, Fe (not more than 0.3 weight%), Al (not more than 0.01 weight%),  
30 and Si (not more than 0.01 weight%) may be cited.

In the leadless copper-based alloys conforming to this invention, the Cu-Sn-Zn-Bi-Se- and the Cu-Sn-Zn-Bi-based bronze cast alloys containing Te and Zr as added elements were tested for tensile strength. The results of the test will be described below.

The tensile test was performed on a test piece No. 4 specified in JIS (Japanese Industrial Standard) Z2201 and manufactured by casting a given sample in a CO<sub>2</sub> mold at a casting temperature of 1130°C in accordance with the JIS A Plan and cutting the resultant molding alloy by using an Amsler's tensile tester. This tensile test was carried out on individual samples of n = 4. The test results reported are averages of the numerical values found for these samples.

The four tensile tests were carried out each under the following four conditions.

(Test 1)

Te content: 0 to 1.48 weight%, Testing temperatures: room temperature (22°C), 100°C and 150°C. The compositions of samples were as shown in Table 1. This test 1 was intended to confirm the effect of the Te content.

Table 1

Sample		Chemical analyses (unit: weight%)							
		Cu	Zn	Sn	Bi	Se	Pb	P (ppm)	Te
Comp. Example	No. 1	86.3	8.16	4.16	1.17	0.15	0.005	194	0
This invention	No. 2	85.9	8.28	4.36	1.19	0.19	0.006	199	0.04
This invention	No. 3	86.1	8.33	4.19	1.17	0.19	0.004	182	0.11
This invention	No. 4	86.0	8.30	4.28	1.22	0.18	0.004	193	0.16
This invention	No. 5	85.7	8.06	4.17	1.28	0.20	0.005	232	0.50
This invention	No. 6	85.1	8.27	4.09	1.30	0.20	0.004	190	0.99
This invention	No. 7	84.7	8.14	4.11	1.32	0.21	0.004	216	1.48

(Test 2)

Te content: 0 to 0.17 weight%, Se content: 0 to 1.2 weight%, Testing temperature: 150°C. The compositions of samples were as shown in Table 2. This test 2 was intended to confirm the effect of the Te content by using samples of varied Se contents.



Table 2

Sample		Chemical analyses (unit: weight%)							
		Cu	Zn	Sn	Bi	Se	Pb	P (ppm)	Te
Comp. Example	No. 8	86.4	8.30	3.91	1.2	0	0.0105	196	0
Comp. Example	No. 9	85.9	8.18	4.24	1.38	0.21	0.0094	207	0
Comp. Example	No. 10	85.6	8.32	4.21	1.36	0.42	0.0121	216	0
Comp. Example	No. 11	85.2	8.50	4.13	1.41	0.65	0.0095	190	0
Comp. Example	No. 12	85.1	8.14	4.05	1.4	1.18	0.0099	230	0
This invention	No. 13	86.4	8.32	3.98	1.25	0	0.0096	209	0.06
This invention	No. 14	85.8	8.30	4.12	1.34	0.22	0.0112	201	0.06
This invention	No. 15	85.3	8.30	4.27	1.48	0.50	0.0106	218	0.04
This invention	No. 16	85.7	8.24	4.02	1.36	0.60	0.008	208	0.05
This invention	No. 17	85.3	8.21	3.91	1.42	1.13	0.0092	223	0.06
This invention	No. 18	86.4	8.30	3.98	1.21	0.01	0.0097	206	0.11
This invention	No. 19	86.2	8.22	4.02	1.27	0.21	0.0105	226	0.1
This invention	No. 20	86.0	8.16	4.02	1.3	0.43	0.0135	205	0.12
This invention	No. 21	86.2	7.99	3.96	1.22	0.58	0.0104	203	0.1
This invention	No. 22	84.9	8.38	4.09	1.36	1.20	0.0162	216	0.11
This invention	No. 23	86.6	8.35	3.82	1.23	0	0.0147	208	0.14
This invention	No. 24	86.5	7.95	4.03	1.27	0.21	0.0055	208	0.14
This invention	No. 25	85.7	8.14	4.25	1.36	0.42	0.0144	207	0.15
This invention	No. 26	85.5	8.25	4.08	1.43	0.64	0.0141	213	0.17
This invention	No. 27	85.0	8.17	4.16	1.41	1.18	0.0118	225	0.15

(Test 3)

Te content: 0 to 0.22 weight%, Se content: 0 to 0.83 weight%, Zn content: 1.02 to 8.53 weight%, Testing temperature: 150°C. The compositions of samples were as shown in Table 3. This test 3 was intended to confirm application to low Zn.

Table 3

Sample		Chemical analyses (unit: weight%)							
		Cu	Zn	Sn	Bi	Se	Pb	P (ppm)	Te
Comp. Example	No. 28	91.8	1.90	4.57	1.72	0.01	0.0211	182	0
This invention	No. 29	91.8	1.93	4.46	1.73	0.00	0.0200	203	0.12
This invention	No. 30	91.8	1.71	4.61	1.82	0.45	0.0188	153	0.21
Comp. Example	No. 31	91.2	1.97	4.59	1.79	0.45	0.0175	210	0
This invention	No. 32	91.2	1.99	4.34	1.76	0.43	0.0165	238	0.10
This invention	No. 33	92.4	1.02	4.54	1.81	0.82	0.0267	146	0.21
Comp. Example	No. 34	91.4	1.44	4.43	1.79	0.79	0.0271	211	0
This invention	No. 35	91.3	1.76	4.42	1.68	0.83	0.0169	278	0.09
This invention	No. 36	91.4	1.48	4.57	1.83	0.02	0.0169	226	0.22
Comp. Example	No. 37	90.1	3.58	4.62	1.69	0.01	0.0180	234	0
This invention	No. 38	90.2	3.44	4.47	1.66	0.01	0.0185	229	0.12
This invention	No. 39	90.1	3.66	4.57	1.63	0.38	0.0260	206	0.22
Comp. Example	No. 40	89.6	3.73	4.42	1.72	0.41	0.0186	234	0
This invention	No. 41	89.8	3.70	4.54	1.63	0.41	0.0155	225	0.13
This invention	No. 42	89.6	3.80	4.42	1.62	0.78	0.0162	242	0.21
Comp. Example	No. 43	89.8	3.25	4.39	1.69	0.75	0.0209	217	0
This invention	No. 44	89.4	3.66	4.52	1.70	0.77	0.0142	242	0.12
This invention	No. 45	89.2	3.71	4.54	1.71	0.01	0.0174	210	0.20
Comp. Example	No. 46	85.8	8.12	4.56	1.48	0.00	0.0168	246	0
This invention	No. 47	85.4	8.53	4.22	1.42	0.00	0.0150	232	0.10
This invention	No. 48	86	8.45	4.51	1.27	0.33	0.101	226	0.22
Comp. Example	No. 49	85.1	8.45	4.42	1.53	0.32	0.143	264	0
This invention	No. 50	85.4	8.38	4.42	1.45	0.28	0.139	261	0.11
This invention	No. 51	85.5	8.36	4.54	1.35	0.28	0.123	249	0.22
Comp. Example	No. 52	84.9	8.38	4.54	1.54	0.60	0.137	262	0
This invention	No. 53	85	8.34	4.43	1.51	0.64	0.139	262	0.13
This invention	No. 54	85	8.26	4.51	1.56	0.58	0.142	277	0.21

(Test 4)

- Zr content: 0 to 0.21 weight%, Testing temperature: room temperature (20°C),  
5 100°C and 150°C. The compositions of samples were as shown in Table 4. This test 4 was intended to confirm the effect of Zr content.

Table 4

Sample		Chemical analyses (unit: weight%)							
		Cu	Zn	Sn	Bi	Se	Pb	P (ppm)	Zr
Comp. Example	No. 55	86.9	7.47	4.00	1.31	0.17	0.054	212	0
This invention	No. 56	86.3	8.28	3.92	1.25	0.18	0.048	258	0.05
This invention	No. 57	86.4	8.00	4.05	1.21	0.17	0.052	239	0.12
This invention	No. 58	86.2	7.87	4.05	1.37	0.18	0.057	253	0.21

The results of the test 1 are shown in Table 5 and Fig. 1. From these results, it is noted that the samples having Te contents of 0.04 weight%, 0.11 weight%, 0.16 weight%, 0.50 weight%, 0.99 weight% and 1.48 weight% acquired improvements respectively of 198.3 N/mm<sup>2</sup>, 210.1 N/mm<sup>2</sup>, 218.6 N/mm<sup>2</sup>, 215.9 N/mm<sup>2</sup>, 202.3 N/mm<sup>2</sup> and 197.7 N/mm<sup>2</sup> in tensile strength at 100°C as compared with the standard of 175.7 N/mm<sup>2</sup>, and improvements respectively of 168.0 N/mm<sup>2</sup>, 185.5 N/mm<sup>2</sup>, 209.7 N/mm<sup>2</sup>, 208.5 N/mm<sup>2</sup>, 195.1 N/mm<sup>2</sup> and 194.8 N/mm<sup>2</sup> in tensile strength at 150°C as compared with the standard of 155.4 N/mm<sup>2</sup>. The results indicate that the containment of Te results in imparting sufficient tensile strength at room temperature and allowing the tensile strength to be enhanced at elevated temperatures. Since the content exceeding 1.0 weight% does not favor economy, the Te contents were invariably set below 1 weight%. As shown in Table 5 and in Fig. 1, the tensile strength at elevated temperatures reached the maximum when the Te content was 0.16 weight%.

Table 5

Sample	Temperature	Tensile strength (N/mm <sup>2</sup> )
No. 1	Room temperature (22°C)	226.4
	100°C	175.7
	150°C	155.4
No. 2	Room temperature (22°C)	228.0
	100°C	198.3
	150°C	168.0
No. 3	Room temperature (22°C)	230.2
	100°C	210.1
	150°C	185.5
No. 4	Room temperature (22°C)	225.5
	100°C	218.6
	150°C	209.7
No. 5	Room temperature (22°C)	220.2
	100°C	215.9
	150°C	208.5
No. 6	Room temperature (22°C)	204.2
	100°C	202.3
	150°C	195.1
No. 7	Room temperature (22°C)	200.1
	100°C	197.7
	150°C	194.8

The results of the test 2 are shown in Table 6 and Fig. 2. Incidentally, Se = 0, 0.2 weight%, 0.4 weight%, 0.6 weight% and 1.2 weight% were invariably target values.

- 5 From the results, it is noted that the samples No. 8, 13, 18 and 23 having Te contents of 0, 0.06 weight%, 0.11 weight% and 0.14 weight% respectively acquired improvements of 104.7 N/mm<sup>2</sup>, 109.1 N/mm<sup>2</sup>, 118.9 N/mm<sup>2</sup> and 124.6 N/mm<sup>2</sup> in tensile strength when Se = 0, that the samples No. 9, 14, 19 and 24 having Te contents of 0, 0.06 weight%, 0.11 weight% and 0.14 weight% respectively acquired more improvements of 150.0 N/mm<sup>2</sup>, 10  
10 150.7 N/mm<sup>2</sup>, 161.8 N/mm<sup>2</sup> and 167.3 N/mm<sup>2</sup> in tensile strength when Se = 0.2 than when Se = 0, that the samples No. 10, 15, 20 and 25 having Te contents of 0, 0.04 weight%, 0.12 weight% and 0.15 weight% respectively acquired improvements of 146.7 N/mm<sup>2</sup>, 148.2 N/mm<sup>2</sup>, 185.5 N/mm<sup>2</sup> and 204.7 N/mm<sup>2</sup> in tensile strength when Se = 0.4, that the samples No. 11, 16, 21 and 26 having Te contents of 0, 0.05 weight%, 0.10  
15 weight% and 0.17 weight% respectively acquired improvements of 159.6 N/mm<sup>2</sup>, 156.4 N/mm<sup>2</sup>, 188.0 N/mm<sup>2</sup> and 204.4 N/mm<sup>2</sup> in tensile strength when Se = 0.6, and that the samples No. 12, 17, 22 and 27 having Te contents of 0, 0.06 weight%, 0.11 weight% and 0.15 weight% respectively acquired improvements of 163.5 N/mm<sup>2</sup>, 176.6 N/mm<sup>2</sup>, 201.2

N/mm<sup>2</sup> and 215.3 N/mm<sup>2</sup> in tensile strength when Se = 1.2. These results indicate that the tensile strength improved in accordance as the Te content increased. This fact shows that the tensile strength at elevated temperatures was improved by increasing the Se content besides containing Te.

5

Table 6

Sample	Tensile strength (N/mm <sup>2</sup> )
No. 8	104.7
No. 9	150.0
No. 10	146.7
No. 11	159.6
No. 12	163.5
No. 13	109.1
No. 14	150.7
No. 15	148.2
No. 16	156.4
No. 17	176.6
No. 18	118.9
No. 19	161.8
No. 20	185.5
No. 21	188.0
No. 22	201.2
No. 23	124.6
No. 24	167.3
No. 25	204.7
No. 26	204.4
No. 27	215.2

Particularly as shown in Fig. 2, the sample having a Se content of 0.2 weight% showed an improvement of about 50% in tensile strength at elevated temperatures relative to the sample given absolutely no Se content and the sample having a Te content of not less than 0.05 weight% showed a further improvement in tensile strength at elevated temperatures. While the tensile strength at elevated temperatures improved in accordance as the Se content increased, this improvement had a moderate inclination. The present example, the upper limit of the Se content was fixed at 1.2 weight% from the viewpoint of economy. When the ratio of this improvement in tensile strength is taken into account, the upper limit is preferably at 0.4 weight% and optimally at 0.2 weight%.

The results of the test 3 are shown in Table 7 and Fig. 3 through Fig. 5. Incidentally, Zn = 2 weight%, 4 weight% and 8 weight%, Se = 0, 0.3 weight% and 0.6 weight% were invariably target values. From these results, it is noted that on the level of

Zn = 2, the samples No. 28 to No. 30 having Te contents of 0, 0.12 weight% and 0.21 weight% showed tensile strengths respectively of 121.4 N/mm<sup>2</sup>, 150.7 N/mm<sup>2</sup> and 155.5 N/mm<sup>2</sup>, that when Se = 0.3, the samples No.31 to No. 33 having Te contents of 0, 0.10 weight% and 0.21 weight% showed tensile strengths respectively of 170.4 N/mm<sup>2</sup>, 198.7 N/mm<sup>2</sup> and 200.4 N/mm<sup>2</sup> and that when Se = 0.6, the samples No. 34 to No. 36 having Te contents of 0, 0.09 weight% and 0.22 weight% showed tensile strengths respectively of 154.1 N/mm<sup>2</sup>, 198.0 N/mm<sup>2</sup> and 215.8 N/mm<sup>2</sup>, indicating that the tensile strength improved in accordance as the Se and Te contents increased. Even at the levels of Zn = 4 weight% (samples No. 37 to No. 45) and 8 weight% (samples No. 46 to No. 54), the improvements in tensile strength in consequence of the increases of Te content when Se = 0 were smaller than when Se = 0.3 weight% and 0.6 weight%, whereas the tensile strengths improved in consequence of the increases in the Se and Te contents when Se = 0.3 weight% and 0.6 weight%. This fact indicates that the tensile strength at elevated temperatures was improved by increasing the Se content besides containing Te similarly to the test 2. As shown in Table 7 and Fig. 3 through Fig. 5, the application of this invention was effective even when the Zn content was low.

Table 7

Sample	Tensile strength (N/mm <sup>2</sup> )
No. 28	121.4
No. 29	150.7
No. 30	155.5
No. 31	170.4
No. 32	198.7
No. 33	200.4
No. 34	154.1
No. 35	198.0
No. 36	215.8
No. 37	117.1
No. 38	161.1
No. 39	174.6
No. 40	144.2
No. 41	191.3
No. 42	206.9
No. 43	162.3
No. 44	200.7
No. 45	220.4
No. 46	120.5
No. 47	128.1
No. 48	156.1
No. 49	155.0
No. 50	163.8
No. 51	196.9
No. 52	156.5
No. 53	187.0
No. 54	217.6

The results of the test 4 are shown in Table 8 and Fig. 6. From these results, it is noted that the samples having Zr contents of 0.05 weight%, 0.12 weight% and 0.21 weight% showed improved tensile strengths of 180.1 N/mm<sup>2</sup>, 194.7 N/mm<sup>2</sup> and 205.6 N/mm<sup>2</sup> at 100°C as compared with the standard tensile strength of 170.4 N/mm<sup>2</sup> and showed improved tensile strengths of 157.8 N/mm<sup>2</sup>, 172.0 N/mm<sup>2</sup> and 184.2 N/mm<sup>2</sup> at 150°C as compared with the standard tensile strength of 149.4 N/mm<sup>2</sup>. At the room temperature, since the tensile strength was not fluctuated by the Zr content similarly to Te, the samples invariably possessed sufficient tensile strength. This fact indicates that also by the containment of Zr, fully sufficient tensile strength was acquired at the room temperature and the tensile strength was further enhanced at elevated temperatures. From the foregoing test, it has been clarified that the containment of Te enabled the tensile strength at elevated temperatures to be improved and further the interaction of Te with Se

enabled the tensile strength at elevated temperature to be improved. The containment of Zr also enabled the tensile strength at elevated temperatures to be improved, though this effect was slightly lower than Te.

5

Table 8

Sample	Temperature	Tensile strength (N/mm <sup>2</sup> )
No. 55	Room temperature (22°C)	223.1
	100°C	170.4
	150°C	149.4
No. 56	Room temperature (22°C)	220.6
	100°C	180.1
	150°C	157.8
No. 57	Room temperature (22°C)	225.3
	100°C	194.7
	150°C	172.0
No. 58	Room temperature (22°C)	219.7
	100°C	205.6
	150°C	184.2

Then, a cutting test was performed for the purpose of rating the machinability due to the addition of Te.

10 The cutting test was performed on the conventional material, the Te-containing product conforming to this invention and CAC406. The chemical analyses of the samples are shown in Table 9.

Table 9

Sample		Chemical analyses (unit: weight%)							
		Cu	Zn	Sn	Bi	Se	Pb	P (ppm)	Te
Comp. Example	No. 59	85.9	8.28	4.36	1.25	0.20	0.006	193	-
This invention	No. 60	85.4	8.33	4.19	1.31	0.19	0.004	188	0.51
CAC406	No. 61	84.6	5.75	4.26	-	-	5.38	202	-

15 The cutting test was carried out under the conditions of 30 mm in processing diameter, 0.2 mm/rev in feed rate, 3.0 mm in depth of cut, 1800 rpm in rotational frequency, 170 m/min in cutting speed, and dry cutting state. The test results were rated by determining the cutting resistances offered by the individual samples and reporting them as indexes of machinability based on the cutting resistance offered by CAC406 taken as 100. The method for determining the index of machinability is shown below.

20 Index of machinability = (Numerical value of cutting resistance offered by CAC406)/(Numerical value of cutting resistance offered by a given sample) x 100



The results of the test for machinability are shown in Table 10 and Fig. 7. From these results, it is noted that the index of machinability of the Comparative Example was 84.4 and that of the sample having a Te content of 0.51 weight% was 95.1, indicating that the containment of Te resulted in greatly enhancing the machinability.

5

Table 10

Sample		Index of machinability
Comp. Example	No. 59	84.4
This invention	No. 60	95.1
CAC406	No. 61	100

Then, in the copper-based alloys conforming to this invention, the examples inclusive of test examples of the Cu-Sn-Zn-Bi-Se-based bronze alloy containing P as an additive element and the examples inclusive of test examples of the Cu-Sn-Zn/Bi-Se-based bronze alloy containing Te as an additive element will be described below.

The bronze cast alloys containing P as an additive element in ratios of 0.05 to 0.09 weight% and the bronze cast alloys containing Te in ratios of 0.1 to 0.21 weight%, both based on the Cu-Sn-Zn-Bi-Se-based bronze alloy were prepared. These bronze cast alloys were tested for high temperature using the Charpy impact test. The results of the test will be described. The contents of Pb in the bronze cast alloys mentioned above were kept below 0.2 weight%.

For the Charpy impact test, test pieces No. 3 specified in JIS Z2202 and manufactured by casting a given alloy in a CO<sub>2</sub> mold at a casting temperature of 1130°C and subjecting the products of casting to a machining process and a Charpy impact tester (300 J) specified in JIS B7722 were used. An oil bath was used for the test. A given test piece was heated to 100°C with the oil in the bath heated in advance to elevated temperatures, retained at the temperature for 10 minutes, taken out of the oil bath, and made to undergo the Charpy impact test within 5 seconds.

Table 11 shows the chemical compositions of the individual test pieces and Table 12 shows the magnitudes of the impact (ratios relative to the standard) found in the samples containing P in a ratio of 0.05 weight% (Sample No. 62) and 0.09 weight% (Sample No.63) relative to the magnitude of the impact found in the standard sample (Sample No. 64). The data of these samples No. 62 to No. 64 plotted in a graph are shown in Fig. 8.

Table 11

Sample		Chemical analyses (unit: weight%)							
		Cu	Zn	Sn	Bi	Se	Pb	P	Te
This invention	No. 62	86.90	7.42	3.90	1.28	0.15	0.20	0.05	-
This invention	No. 63	86.70	7.74	3.90	1.19	0.15	0.19	0.09	-
Comp. Example	No. 64	86.80	7.66	3.80	1.34	0.16	0.18	0.02	-
This invention	No. 65	86.90	7.72	3.74	1.26	0.16	0.20	0.02	0.10
This invention	No. 66	87.00	7.54	3.87	1.18	0.17	0.19	0.02	0.21
Comp. Example	No. 67	87.00	7.55	3.84	1.23	0.15	0.19	0.02	-

Table 12 shows the magnitudes of the impact found in the samples containing Te in a ratio of 0.1 weight% (Sample No. 65) and 0.21 weight% (Sample No. 66) relative to the magnitude of the impact found in the standard sample (Sample No. 67) taken as 100. The data of these samples No.65 to No. 67 plotted in a graph are shown in Fig. 9.

Table 12

Sample		Area ratio of Pi-Pb eutectic crystal (%)	Ratio of magnitude of impact to standard (%)
This invention	No. 62	0.103	126
This invention	No. 63	0.104	273
Comp. Example	No. 64	0.268	100
This invention	No. 65	0.052	175
This invention	No. 66	0.035	248
Comp. Example	No. 67	0.212	100

As shown in Fig. 8, the containment of P in a ratio of 0.05 weight% resulted in enhancing the magnitude of impact to 126% relative to the standard sample and the containment of P in a ratio of 0.09 weight% resulted in enhancing the magnitude of impact to 273% relative to the standard sample. Thus, it has been found that the magnitude of impact of alloy was enhanced in consequence of the containment of P.

As shown in Fig. 9, the containment of Te in a ratio of 0.1 weight% resulted in enhancing the magnitude of impact to 175% relative to the standard sample and the containment of Te in a ratio of 0.21 weight% resulted in enhancing the magnitude of impact to 248% relative to the standard sample. Thus, it has been found that the magnitude of impact of alloy was enhanced in consequence of the containment of Te similarly to the containment of P.

As a result of the test for impact at elevated temperatures, the containment of P resulted in enhancing the magnitude of impact to an average of 200% and the

containment of Te resulted in enhancing the magnitude of impact to an average of 212% relative to the standard sample.

Incidentally, the area ratios of the Bi-Pb eutectic crystal shown in the same table and the same diagrams will be described afterward.

5 The individual test pieces were further subjected to the EDX quantitative analysis and the mapping.

The term “mapping” refers to an action of analyzing a given sample to find the sites of presence of a specific element. It shows the portion in which the element concentrically exists in a yellow color. This analysis was carried out on a cut surface so  
10 formed as to avoid a fracture plane in a test piece that undergone the Charpy impact test. A metallographic photograph (400 magnifications) of a new standard sample (comparative example) is shown in Fig. 10. The mapping of the individual elements found in the metallographic photograph of Fig. 10 is shown in Fig. 11.

The chemical composition of this standard sample (Comparative Example) is  
15 shown in Table 13 and the results of the EDX quantitative analysis performed in the regions 1 to 3 shown in the metallographic photograph of Fig. 10 are shown in Table 14.

Table 13

Chemical analyses (unit: weight%)						
Cu	Zn	Sn	Bi	Se	Pb	Cr
87.0	7.78	3.53	1.27	0.15	0.21	Less than 0.005

20 Table 14

	Chemical analyses (unit: weight%)						
	Cu	Zn	Sn	Bi	Se	Pb	Cr
Area 1	5.63	2.39	0.50	44.31	0.18	46.98	0.00
Area 2	2.84	0.52	0.13	96.50	0.01	0.00	0.00
Area 3	3.81	45.66	0.15	0.00	50.27	0.08	0.02

It is clear from Fig. 11 and Table 14 that the coexistence of Bi and Pb in the area 1 is evident from the mapping results of the standard sample shown in Fig. 11 and that the fact that Bi and Pb are concentrated in the area 1 and give rise to a Bi-Pb binary eutectic  
25 crystal is evident from the results of the EDX quantitative analysis shown in Table 14.

Then, the metallographic photograph (400 magnifications) of the sample NO. 63 containing P in a ratio of 0.09 weight% is shown in Fig. 12 and the mapping of the individual elements appearing in the metallographic photograph of Fig. 12 is shown in

Fig. 13. The results of the EDX quantitative analysis performed in the areas 1 and 2 appearing in the metallographic photograph of Fig. 12 are shown in Table 15.

Table 15

	Chemical analyses (unit: weight%)						
	Cu	Zn	Sn	Bi	Se	Pb	P
Area 1	2.69	45.98	0.02	0.00	51.01	0.24	0.06
Area 2	6.28	1.15	0.06	92.34	0.14	0.00	0.03

It is clear from Fig. 13 and Table 15 that the mapping shown in Fig. 13 indicates the coexistence of P and Pb in the area 1 and that the results of the EDX quantitative analysis shown in Table 15 indicate the fact that P and Pb formed a P-Pb intermetallic compound concentrically in the area 1.

The term “alloy” as used herein refers to a state in which not less than two kinds of metallic elements are interfused in a solid state. Then, the term “intermetallic compound” refers to a compound that is formed by the union of not less than two component metals in an alloy in a comparatively simple ratio of numbers of atoms.

The metallographic photograph (400 magnifications) of the sample No. 66 containing Te in a ratio of 0.21 weight% is shown in Fig. 14 and the mapping of the individual elements appearing in the metallographic photograph of Fig. 14 is shown in Fig. 15. The results of the EDX quantitative analysis, performed in the areas 1 to 5 appearing in the metallographic photograph of Fig. 14, are shown in Table 16.

Table 16

	Chemical analyses (unit: weight%)						
	Cu	Zn	Sn	Bi	Se	Pb	Te
Area 1	3.40	43.72	0.00	4.22	43.97	0.26	4.43
Area 2	19.22	1.70	2.24	76.44	0.40	0.00	0.00
Area 3	43.05	0.27	0.00	10.76	0.38	3.16	42.37
Area 4	24.08	19.75	0.00	2.40	3.56	1.65	48.56
Area 5	5.57	0.67	0.15	4.15	0.12	53.27	36.08

It is clear from Fig. 15 and Table 16 that the results of the mapping shown in Fig. 15 reveal the coexistence of Te and Pb in the areas 1, 3, 4 and 5 and that the results of the EDX quantitative analysis shown in Table 16 reveal the fact that Te and Pb concentrically formed a Te-Pb intermetallic compound in the areas mentioned above, particularly in the area 5.

For the purpose of determining the ratio of the areas of a Bi-Pb binary eutectic crystal, the metallographic photograph was entrapped and analyzed by the image analyzing software.

5 The term “ratio of areas” refers to the ratio of an area occupied by a target (the Bi-Pb binary eutectic phase) to the area of the field of view formed of the entrapped image.

The Bi-Pb binary eutectic phase was identified through comparison between the results of the EDX quantitative analysis and the metallographic photograph. The metallographic photograph was obtained in 400 magnifications and the ratio of areas was obtained by calculating the average values of 20 fields of vision of each of the samples.

10 The texture observation photographs (before and after image processing) portraying the ratios of areas of the standard sample (sample No. 64), the sample No. 62 containing P in a ratio of 0.05 weight% and the sample No. 63 containing P in a ratio of 0.09 weight% are shown in Fig. 16. The results of the determination of the ratios of areas of the Bi-Pb binary eutectic crystal formed in the case of containing P as an additive  
15 element are shown in Table 11.

The texture observation photographs (before and after image processing) portraying the ratios of areas of the standard sample (sample No. 67), the sample No. 65 containing Te in a ratio of 0.1 weight% and the sample No. 66 containing Te in a ratio of 0.21 weight% are shown in Fig. 17. The results of the determination of the ratios of areas  
20 of the Bi-Pb binary eutectic crystal formed in the case of containing Te as an additive element are shown in Table 12.

As shown in Table 12, the ratio of areas of the Bi-Pb phase of the standard sample (sample No. 64) was 0.268% and the ratio of areas of the Bi-Pb phase containing P was 0.103% when the P content was 0.05 weight% and 0.104% when the P content was 0.09  
25 weight%. The data of these samples No. 62 to No. 64 plotted in a graph is shown in Fig. 8.

As shown in Table 12, the ratio of surfaces of the Bi-Pb phase of the standard sample (the sample No. 67) was 0.212% and the ratio was 0.052% when the Te content was 0.1 weight% and 0.035% when the Te content was 0.21 weight%. The data of these  
30 samples No. 65 to 67 plotted in a graph are shown in Fig. 9.

Fig. 8 and Fig. 9 reveal that the containment of P and Te as additive elements resulted in suppressing the ratio of areas of the Bi-Pb phase below 0.2%. They also reveal that the suppression of the occurrence of the Bi-Pb binary eutectic crystal

particularly below 0.1% resulted in enhancing the magnitude of impact to about 130% as compared with the standard sample.

In consequence of the test for impact at elevated temperatures, the EDX quantitative analysis, the mapping and the determination of the ratio of areas of the Bi-Pb binary eutectic crystal, the containment of P and Te resulted in forming the P-Pb intermetallic compound and the Te-Pb intermetallic compound in the alloy texture and suppressing the occurrence of the Bi-Pb binary eutectic crystal. Further, it resulted further in enhancing the magnitude of impact at elevated temperatures as evinced by the fact that these intermetallic compounds had high melting points.

Incidentally, the copper-based alloy contemplated by this invention does not need to be restricted to the bronze alloy described above. This invention can be further applied to leadless copper-based alloys including a brass-based alloy, such as a hot forging brass having a Cu content of 59.0 to 62.0 weight%, an Sn content of 0.5 to 1.5 weight%, a Bi content of 1.0 to 2.0 weight%, an Se content of 0.03 to 0.20 weight%, an Fe content of 0.05 to 0.20 weight% and a P content of 0.05 to 0.10 weight% and a brass for machining having a Cu content of 61.0 to 63.0 weight%, an Sn content of 0.3 to 0.7 weight%, a Bi content of 1.5 to 2.5 weight%, an Se content of 0.03 to 0.20 weight%, an Fe content of 0.1 to 0.30 weight% and a P content of 0.05 to 0.10 weight%.

While the preceding examples have been described as suppressing the occurrence of the Bi-Pb binary eutectic crystal in the alloy texture by incorporating the additive elements of Te and P, this invention allows, during the course of casting a copper-based alloy, to decrease the amount of a recycled material, such as scrap, to be used and adjust the amount of Pb contained as an unavoidable impurity to a level further below the upper limit of 0.2 weight%.

#### Industrial Applicability:

According to this invention, by incorporating additive elements capable of forming an alloy or an intermetallic compound with Bi and Pb existing either independently or a mutually joined state, it is made possible to suppress the occurrence of the Bi-Pb binary eutectic crystal in the alloy texture and consequently mend the deterioration of mechanical properties, particularly tensile strength, at elevated temperature.

The copper-based alloy of this invention is suitable for processing and molding water-contacting products, such as valves, joints, pipes, water taps, and articles for supply of cold water and hot water and for processing and molding electro-mechanic products, such as gas utensils, washing machines and air conditioners.

5            Besides, the copper-based alloy according to this invention can be advantageously applied extensively to members and parts, such as water-contacting parts like valves and water taps, specifically ball valves, balls in ball valves, butterfly valves, gate valves, globe valves, check valves, faucets, hot water supplying devices, mounting brackets for  
10 fittings, refrigerant tubes, parts (casings, gas nozzles, pump parts and burners) for electric water warming devices, strainers, parts for water way meters, underwater and sewage parts, waste water plugs, elbow pipes, bellows, connecting flanges for toilet seats, spindles, joints, headers, branching plugs, hose nipples, metallic pieces for faucets, water stop plugs, articles for service water and drain supplying plugs, metallic pieces for  
15 sanitary ceramic products, connecting metal pieces for showering hoses, gas utensils, building materials like doors and knobs, household products, adapters for sheath tube headers, parts for automobile coolers, fishing parts, parts for microscopes, parts for city water meters, parts for meters, parts for railroad pantagraphs, and other members and parts. It can be applied extensively to materials, intermediate products, finished products  
20 and assembled bodies of toilet articles, kitchen articles, bathroom articles, washroom articles, articles of furniture, living room articles, parts for sprinklers, parts for doors, parts for gates, parts for automatic vending machines, parts for washing machines, parts for air conditioners, parts for gas welding machines, parts for heat exchangers, parts for solar heat water heating devices, metal dies and parts therefor, bearings, toothed gears,  
25 parts for construction equipment, parts for railroad vehicles and parts for transportation machines.